明治大学外国人研究者招聘制度　報告書

＜招聘教授・研究員の情報 / Guest Professor・Guest Scholar＞

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現在の職名 Position	PhD researcher
招聘期間（日本への入国日から出国日） Invitation Period (from the date of entry to departure)	01/10/2025-03/11/2025
専攻 Field of Research	Chemistry
ホスト教員氏名と所属学部研究科等 Name of host teacher and affiliation at Meiji University	Kazukuni Tahara, Professor, Ph. D.> Department Chair> Department of Applied Chemistry, > School of Science and Technology

＜外国人研究者からの報告 / Foreign Researcher Report＞

①研究課題　/　Research Theme

Merging Covalent Organic Frameworks and Covalently Functionalized 2D Carbon Surfaces: from Structure to Function

②研究概要　/　Outline of Research

Our group (Prof. De Feyter) and the group of Prof. Tahara have a long-standing and multifaceted collaboration. As part of my PhD, I am using a technique that was developed in Prof. Tahara's group. This technique, known as patterned grafting, is described in the following paper: J. Am. Chem. Soc. 2020, 142 (16), 7699-7708.

In summary, Highly Oriented Pyrolytic Graphite (HOPG) is covalently modified via diazonium chemistry in the presence of a template. In the case of the paper mentioned above, the template is a self-assembled molecular network (SAMN) formed from dehydrobenzo[12]annulene (DBA) derivatives, which create a porous network. Radicals formed through the electrochemical reduction of the diazonium salt attach to the HOPG surface only where the pores of the SAMN are present.

The paper also demonstrates the creation of a homochiral, covalently modified, patterned HOPG surface. This was achieved using a chiral DBA derivative as a template (note: the diazonium salt used was still achiral).

Our groups are now further investigating the potential of this technique. One avenue is the production of (chiral) covalently modified patterned HOPG surfaces using alternative templates beyond the DBA derivatives. Another line of investigation is the memory effect—a phenomenon in which the (chiral) covalently modified patterned HOPG surface can influence the self-assembly of subsequently added molecules.

For example, the paper shows that the SAMN of chiral DBA derivatives can form pores with either clockwise or counterclockwise orientation, depending on the enantiomer used. Using a single enantiomer results in a homochiral covalently modified patterned HOPG surface. It is interesting to explore what happens when an achiral DBA derivative is added to this modified surface. If the homochiral surface induces chiral self-assembly of the achiral DBA derivative—resulting in a homochiral SAMN instead of the expected achiral SAMN—this would demonstrate a memory effect.

I have already attempted to reproduce the grafting process described in the J. Am. Chem. Soc. paper. However, some difficulties have been encountered. Successful reproduction requires a homogeneous grafted surface, but so far only non-homogeneous surfaces have been obtained.

Therefore, one of the main aims of this research stay is to further develop my skills in the patterned grafting technique. A second aim is to investigate and explore the memory effect in more detail. These aims are further elaborated below.

1)Fabrication of a homogeneous homochiral nanopatterned surface
Training in Optimizing My Skills in Patterned Grafting

This training can be further divided into several stages. First, scanning tunneling microscopy (STM) will be used to determine the ideal conditions for the formation of the porous self-assembled molecular network (SAMN) of the DBA derivatives. Large domains of the porous network must be formed to ensure effective templating. To identify optimal conditions, the concentration of the DBA template, annealing temperature, and annealing time will be systematically investigated.

Next, the grafting conditions will be optimized. Grafting will be carried out electrochemically using a three-electrode setup and cyclic voltammetry. Key parameters to be studied include the potential range, potential sweep rate, and number of scans.

After electrochemical grafting, the template must be removed. The group of Prof. Tahara has already developed an optimized cleaning procedure, which will be followed.

The resulting covalently modified surfaces will be characterized using Raman spectroscopy and STM to verify the homogeneity of the grafting and confirm the successful removal of the template.

2)Investigating the memory effect
This aim focuses on investigating the influence of the patterned covalently modified surface on the formation of self-assembled molecular networks (SAMNs) or two-dimensional polymers (2DPs).

2.1) Using chiral DBA derivatives as the template

In this method, a homochiral patterned grafted surface will be fabricated using chiral DBA derivatives as the template. The grafting will follow the optimized conditions developed in point 1. Once the grafted surfaces have been characterized via STM, various molecules will be deposited onto the surfaces, and the resulting network formation will be monitored using STM.

Different types of molecules can be used in this step. These include:

·Achiral DBA molecules similar to the chiral ones used for the template
·Achiral DBA molecules with longer alkyl chains
·2DPs (both chiral and achiral)
For these experiments, the drop-casting conditions for each molecule must be investigated. The optimized conditions identified in points 1 and 2 will serve as a starting point for these studies.

For these two points described above, STM will be the primary characterization technique. To obtain statistically meaningful results, a large number of STM images will be required.

明治大学外国人研究者招聘制度　報告書

③招聘期間中の研究活動の実績　/　The research results as Guest Professor・Guest Scholar

1)Fabrication of a homogeneous homochiral nanopatterned surface
The first part of my research stayed focused on creating the nanopatterned surface mentioned above and to improve and optimize my skills.
To obtain this goal, the following grafting procedure was used during my stay in the group of professor Tahara:
The derivative used is called cDBA-OC12-OC12(S). The "S" indicates that the stereocenter of the side chains is the S-enantiomer. This template was dissolved in distilled 1-phenyloctane (1-PO).
Then, 30 μL of a 2.5 μM cDBA-OC12-OC12(S) solution was drop-cast onto highly oriented pyrolytic graphite (HOPG) inside the electrochemical cell (EC cell).
This cell was wrapped in Al foil and placed in an oven at 80 ° C for 3 hours.
After cooling to room temperature, cyclic voltammetry (CV) was performed.
Before the actual CV, the diazonium salt had to be formed in situ. A solution of 4.9 mL containing 0.2 mM trimethoxyaniline dissolved in 50 mM HCl was mixed for 30 seconds with 100 μL of a solution containing 0.1 M $NaNO_2$ dissolved in ultrapure water. This mixing ensured the formation of the diazonium salt. Afterwards, the mixture was carefully added to the EC cell without disturbing the organic templating layer. After a total waiting time of 3 minutes, the CV was performed.
The following parameters were always used: 0.2 V to -0.25 V, 1 scan, and a sweep rate of 0.1 V/s.
For reproducibility, this procedure was conducted on three different HOPG samples using exactly the same method. The three CV cycles all show the same features. When sweeping down in potential, a minimum appears in the graph, corresponding to the reduction of the diazonium salt to its radical form (with the release of N_2). There is no maximum peak when sweeping the voltage back to its original value, indicating that an irreversible process took place. In this case, molecules were irreversibly attached to the surface (covalent functionalization).
After the CV was performed, the samples were further characterized using Raman spectroscopy. The ratio of the intensities of the G-band and D-band indicates whether grafting was successful. The G-band originates from the pristine HOPG surface, while the D-band is a defect-induced band. In this case, the surface defects correspond to the covalently attached moieties. The three different samples show similar ID/IG ratios.
After Raman characterization, STM measurements were conducted. STM images were taken before and after toluene washes. Only sample one was measured before the toluene wash to reduce measurement time, as the pattern created by the grafted moieties should remain after the wash. The purpose of the toluene wash was to remove the template molecules still present on the surface. The bright dots in the image are the covalently attached moieties, while the porous structures correspond to the SAMN of the cDBA-OC12-OC12(S) template.
A 2D-Fast Fourier Transform (2D-FFT) confirmed that pattern transfer occurred from the template to the grafted moieties. The FFT was obtained after filtering the images so that only the grafted moieties remained. The six dots in the 2D-FFT indicate that the grafted species have a hexagonal symmetry, identical to that of the template. This grafted surface is chiral because the template itself is chiral.
Analysis of the CV, Raman, and STM data confirmed that the pattern grafting procedure described in this report is reproducible.
I also conducted three different toluene washes (each wash was done on one of the three samples) to test whether they could successfully remove the template molecules:
After these toluene-washing procedures, the samples were characterized again with Raman and STM. Because the HOPG samples were immersed at elevated temperatures, they showed degrafting. This means that the grafted moieties detached from the surface. This degrafting can be seen in the ID/IG ratios obtained from the Raman spectra.
The three modified HOPG samples still show that the grafting had a pattern (from the 2D-FFT). However, it was also clear that template molecules were still present on the surface and had not been removed by the washing procedures.

2)Investigating the memory effect
Given the chiral nanopatterned surface was reliably fabricated and reproduced, we examined topic two of the research outline in more detail. Although the samples produced in Section 1 indicated that some residual template remains on the surface, they were nonetheless used to evaluate the memory effect.

2.1) Using chiral DBA derivatives as the template

The achiral variant DBA-OC12 (without the additional methyl group in the side chains) was chosen. 10 μL of a 150 μM DBA-OC12 solution in distilled 1-PO was added to the surface and immediately characterized with STM. A high concentration (150 μM vs. 2.5 μM) was used to ensure that the SAMN of DBA-OC12 was linear instead of porous. The STM images show the formation of SAMNs between the grafted moieties and that the linear SAMN polymorph of DBA-OC12 dominates.
When taking smaller-scale STM images, the interdigitation of the DBA-OC12 side chains can be observed. This interdigitation has two enantiomeric forms, referred to as (+)-type and (-)-type interdigitation. If only one type is present on the surface, then the surface exhibits a memory effect. At this moment, there are still too many uncertainties (such as template molecules still present on the surface) to conclude definitively whether a memory effect is present.

3)Conclusion
In conclusion, I have successfully and reproducibly created a chiral, patterned, covalently modified surface. There are still remaining issues concerning the removal of the template with a toluene wash. This will be further investigated in Leuven. The memory effect will also be explored further there.